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ON THE PERMEABILITY OF CAOUTCHOUC FOR VARIOUS SUBSTANCES IN ACETONE SOLUTIONS

By

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Historical.

Experiments in osmosis have been carried on more or less vigorously during the last eighty years by men in various lines of research. Dutroschet and the men who followed him after 1826 worked mainly in the interests of physiology. Graham working in the middle of the nineteenth century used a parchment septum,and thereby separated such things as common salt and silicic acid from each other. He called such a process 'dialysis', a term that is still in vogue; and gave to chemistry the names 'crystalloid' and 'colloid',which,however,have outgrown their usefulness.Moritz Traube (1),the botanist,made and used in 1875 precipitated membranes which were seized upon by Pfeffer in his determinations of osmotic pressures of

aqueous sugar solutions. Copper ferrocyanide was,and has been,the chief,but by no means,the only precipitated membrane in use.Other experimenters proceeded to investigate the permeability of various membranes for a large variety of substances. Naturally caoutchouc came in for its share of attention,but for a certain reason,soon to be mentioned,it was not very popular as a septum until recent years.

In 1866 Payen (2) worked with balloons of rubber,both vulcanized and unvulcanized,which he filled with water and weighed at stated intervals. He found that the water escaped through the unvulcanized rubber about six times as fast as it did through the vulcanized, the exact ratio being 23 to 4. He claimed to have found the rubber,when viewed through a microscope,full of fine holes or pores;and he insisted upon the porosity of the caoutchouc as the explanation of the phenomena.

Thirty years later,Dr.Lundie,aphysician, curious to know why the water beds in the hospitals had to be refilled regularly,also filled and weighed some toy rubber balloons. He too found that they lost water day by day,and under like conditions they lost from fifteen to thirty times as much alcohol as water. While not trying

to put forth a theory of his own, he rejected the porosity theory of Payen, as untenable in the face of the facts. Finally he loaded the balloons with strong solutions of magnesium sulphate and ammonium chloride, and set them into pure water. The sulphate spoiled the experiment by attacking the membrane, but the chloride passed through the rubber in appreciable quantities. (3) It is to be regretted that Dr. Lundie did not test more salts than the two mentioned. It satisfied him to know that india rubber is not strictly waterproof, and that it is permeable to some other things. Alois Zott (4) working with various semi-permeable diaphragms separated a ten percent solution of sodium chloride from pure water by a caoutchouc membrane. In his own words, "Es geht also unter sonst gleichen Verhaeltnissen durch eine duenne Kautschuksmembran nur 1/10 mg. (0.0001 g.) waehrend durch Goldschlaegerhaeutchen one gram NaCl diosmirt." He gave up the use of caoutchouc, and so did many of his contemporaries, who wanted to measure osmotic pressures in dilute aqueous solutions.

The next step was to use non-aqueous solvents and in this field caoutchouc membranes proved very useful to get up osmotic pressures, and to produce results which are not in harmony with the theories of the

'dilute solution' school of physical chemists.

In 1898 Flusin (5) separated a number of organic liquids from each other by means of vulcanized caoutchouc. He took all possible combinations in pairs of the liquids, carbon disulphide, chloroform, acetic acid, toluene, methyl alcohol, petroleum ether, benzyl chloride, xylene, ether, benzol, turpentine, nitrubenzene, and ethyl alcohol. In each case there was a major current from the liquid most readily imbibed by the membrane, through the rubber, to the less readily imbibed liquid. Using the same membrane, Raoult (6) separated methyl alcohol from ether, the main current being from the ether to the alcohol. Guebhard (7) had found some years before an osmose of alcohol through gutta percha into pure water. Kahlenberg (8) tested the permeability of vulcanized caoutchouc membrane when such solvents as water, toluene, benzene, acetic acid, and chiefly pyridine bathed it. He tried various salts, and got up osmotic pressures with them, or found that they passed through the membrane very easily.

So much for the choutchouc. None of the men just mentioned used acetone as one of the liquids in which the septum was bathed, nor did W. Thomsen (9) include it in the list of the forty-four liquids whose effects upon

the elasticity of India rubber he investigated. At the suggestion of Professor Kahlenberg I started a number of experiments with caoutchouc as the membrane, and acetone as the solvent. I wanted to find which of the substances soluble in acetone passed through the caoutchouc into pure acetone, and in a quasi-quantitative way how much passed through in a given time. In this connection it was necessary to know, approximately at least, the solubility of the substances in acetone alone,,and in a mixture of acetone and a hydrocarbon such as kerosene.

Experimental.

To carry out the permeability part of these experiments, an apparatus of the simple character as shown in the drawing was used. The membrane R which was of course the important part of the whole device was tied over the end of a four inch test tube TT, selected with a particularly wide flange. Numerous even windings of white cotton thread held the rubber in place, and insured a firm contact between it and the glass. The folds in the rubber were carefully removed before the winding was completed, and when the latter was accomplished the membrane fit-

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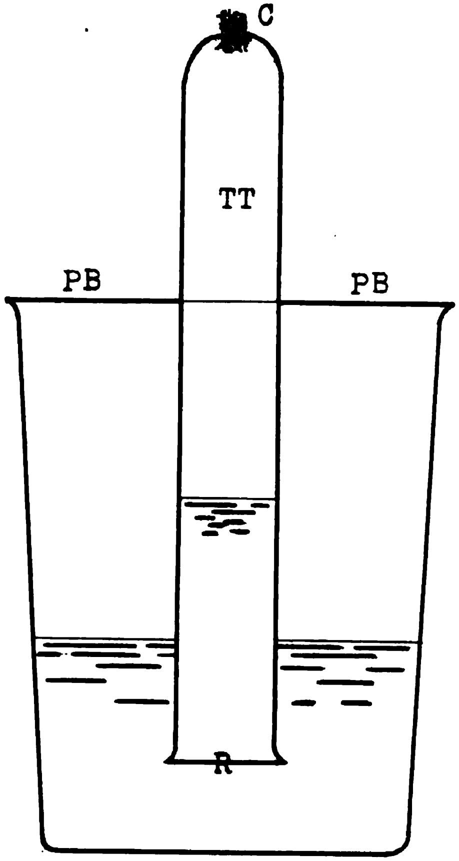


ted smoothly but not too tightly over the end of the test tube. The rest of the apparatus, the beaker, the plug of cotton C, and the pasteboard PB were conveniences in running the experiments, and in preventing undue evaporation of the acetone. No attempt was made to get the inner and outer solutions at the same level to begin with, but the level of each was noted by the label which bore its mark of identification. The membrane was sheet rubber, such as used by dentists for "dams", very elastic and nearly pure gum. The acetone in all cases was dried over anhydrous copper sulphate, and redistilled at a constant temperature of 57°.7. Into the test tube so fitted up were placed from five to ten cubic centimeters of the saturated acetone solution of the substance in question, which was then lowered into the pure acetone in a beaker and allowed to stand for a period of fifteen to twenty hours, after which it was tested as follows. The outer solution, which at the beginning of the experiment was pure acetone, was evaporated in a watch glass, and the residue compared with the residue of the rubber extract obtained when pure acetone was used on both sides of the membrane. The latter was re-

moved from the tube and its condition noted. The substances that had penetrated the rubber most easily would of course leave a considerable residue, while those that had not done so, would leave only a very small residue.

One of the first substances tested was malic acid, CH_2 COOH CHOH COOH. It was soluble 18.05 parts in 100 parts of acetone at 25°.2 but passed through the membrane only with difficulty, and one cc of kerosene threw it out of one cc of its acetone solution. Another was mercuric chloride, $HgCl_2$, soluble 60 parts in 100 parts of acetone at 25°, which passed readily through the membrane and was not thrown out of 1 cc of its acetone solution by 38 cc of kerosene. In all cases, as with malic acid and mercuric chloride, one cubic centimeter of the solution was taken, and kerosene added until the substance was thrown out. Soluble _ _ _ parts at _ _ _ degrees always means soluble _ _ _ parts in 100 parts by weight of acetone. (Degrees Centigrade.)

The theory upon which the whole line of work was based can be explained from the above results. In the first place our membrane is a hydrocarbon, and has affinity for hydrocarbons and for things soluble in them. Bathed on one side in the experiment by pure ace-

tone, and on the other by the acetone solution of malic acid, it imbibed the acetone together with a little malic acid, which, however, had but slight affinity for the hydrocarbon and did not get into it easily. Such as did penetrate the membrane came into contact with the pure acetone on the other side and was washed out of the rubber, because of the superior affinity of the acetone for the malic acid. Kerosene is another hydrocarbon, not an aromatic one as rubber, but a complex mixture of higher hydrocarbons with large molecular weights. On our affinity notions in the question of solubility we would expect that substances soluble in such a hydrocarbon as kerosene would also have affinity for the hydrocarbon rubber, and here in the case of malic acid our expectations are confirmed. This acid has little affinity for kerosene, as evidenced by the fact that only a small quantity of the latter threw it out of its acetone solution: and likewise it passed thr~~ew~~ough a hydrocarbon membrane only sparingly. The rubber did not have affinity for it and did not imbibe very much of it. Hence there was only irregular osmosis in this case.

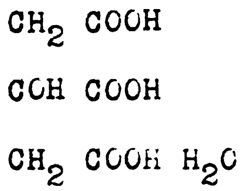
Turning to the mercuric chloride we find a different state of affairs. The membrane imbibed the

acetone and the chloride readily, and the pure acetone on the other side washed the chloride out of the rubber, so that a considerable quantity of it was found in the outer solvent. That $HgCl_2$ has considerable affinity for acetone in the presence of a hydrocarbon is evidenced by the fact that 38 cc of kerosene did not throw it out of its acetone solution. Reviewing the cases just mentioned, we find two substances, one easily thrown out of acetone by kerosene, and passing sparingly through caoutchouc: the other thrown out only with difficulty, and passing through the membrane readily. From the consideration of these results, we are lead to postulate two things, namely that any substance soluble in acetone in the presence of a lot of kerosene will penetrate a septum of vulcanized caoutchouc: and that any substance not so soluble will find its way through such a membrane only sparingly.

Oxalic acid, $(COOH)_2 2H_2O$, from Merck, heated to 110° in an air bath to drive off the water of crystallization soluble 11.7 parts at 25°, was thrown out of solution by 3.6 cc of kerosene, and passed through the rubber with difficulty. It behaved like malic acid.

Succinic acid, $(CH_2\ COOH)_2$, from Kahlbaum, soluble 1.7 parts at 25°, was thrown out of solution with 3 cc of kerosene, and passed through the membrane only sparingly. These three acids then behaved alike in being thrown out from acetone by small amounts of kerosene, and by passing through the vulcanized caoutchouc with difficulty.

Citric acid,



$$\begin{array}{l} CH_2\ COOH \\ COH\ COOH \\ CH_2\ COOH\ H_2O \end{array}$$

from Kahlbaum, soluble 23.1 parts at 25°, thrown out by 28 cc of kerosene, passed through a little more readily than the above acids.

Tartaric acid $(CH\ OH.COOH)_2$, from Schuchardt, soluble 4.4 parts at 25°, went through the septum much like citric acid, and required a large amount of kerosene to separate it from the acetone.

Lithium chloride, LiCl, from E. de Haën, soluble 1.5 parts at 25°, was not thrown out by 53 cc of kerosene, and still passed through the septum only sparingly. This was one of the substances used by Kahlenberg (10) to get up osmotic pressures with pyridine solutions. These

two acids and the chloride did not support our first theoretical consideration, that a substance soluble in acetone in the presence of a lot of kerosene should go through the membrane readily, but as they are not soluble in aromatic hydrocarbons their conduct towards the membrane was not unexpected.

Zinc chloride, $ZnCl_2$, in sticks from Schuchardt, freely soluble in acetone (11), was not thrown out by less than 60 cc of kerosene, and passed readily through the membrane, and this chloride, like mercuric, supported our first theoretical consideration, which parallels solubility in the presence of kerosene with ease of penetration of the caoutchouc membrane.

Cobaltous chloride, $CoCl_2\ 6H_2O$, from Schuchardt, soluble 8.2 parts in acetone (11), penetrated the membrane easily. The color of the solution was deep blue.

Phosphorous trichloride, PCl_3, from Schuchardt, freely soluble in acetone, passed readily through the membrane. The solution colorless at first turned very dark on standing over night.

Antimony trichloride, $SbCl_3$, from E. de Haën,

freely soluble in acetone, passed readily through the membrane. The solution likewise turned dark, and drew its own volume of pure acetone through the membrane to itself.

Ferric Chloride, $FeCl_3$, anhydrous, from E. de Haën, freely soluble in acetone (11), passed readily through the septum. It dissolved in acetone to form at once a dark solution with evolution of heat. It had a disintegrating effect upon the rubber, as also noticed by Kahlenberg (12). Ferric chloride is soluble in hydrocarbons, and hence would be expected to be imbibed by a hydrocarbon membrane. (13)

Potassium iodide, KI, from Schuchardt, soluble 2.93 parts at 25°, (11) passed readily through the membrane.

Mercuric iodide, HgI_2, from E. de Haën, soluble 2 parts at 25°, (11) passed readily through the membrane.

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(12) Cf. in this connection some interesting experiments by Lewis and Thomsen, ChN. 64:169, on the destructive effects of certain salts on caoutchouc.

Silver nitrate, $AgNO_3$, from Henry Heil, soluble in acetone, (11), acted like the iodides above mentioned, while Kahlenberg (14) found that in pyridine solutions, it passed into the outer solvent only in mere traces.

Cadmium bromide, $CdBr_2$, from Eimer and Amend, freely soluble in acetone, passed through the membrane readily. The above named halogen salts of the heavy metals show similarity with regard to their solubility in acetone, and their ease of penetration of the caoutchouc septum. In this connection it may be mentioned that Kahlenberg (15) found that iodine and toluene penetrated and attacked the rubber membrane.

Mercuric cyanide, $Hg(CN)_2$, from Schuchardt, soluble 14.9 parts at 25°, was thrown out of its acetone solution by 1 cc of kerosene and did not find its way through the rubber in notable quantities.

Boric acid, H_3BO_3, c. p. Ph. G.III, cryst., freely soluble in acetone (11), fell out of solution upon the addition of 1 cc of kerosene, and passed through the membrane only sparingly.

Zinc acetate, $Zn(C_2H_3O_2)_2\ 2H_2O$, made in the department of Pharmacy, soluble 1.08 parts in acetone at

25°, after drying at 110° was thrown out of its acetone solution by 1 cc of kerosene and failed to pass readily through the membrane. These three examples support our second theoretical consideration, namely that any substance not easily soluble in acetone in the presence of a lot of kerosene, will pass through a septum of caoutchouc only sparingly.

Lithium salicylate, $Li(C_6H_4OHCOO)$, soluble in acetone passed through fairly readily.

Camphoric acid, $C_8H_{14}(COOH)_2$, from Kahlbaum, freely soluble in acetone, passed through the membrane readily.

Triphenyl methane, $CH(C_6H_5)_3$, from Kahlbaum, soluble in acetone, passed readily through the membrane,

Phthallic anhydride, $C_6H_4(CO)_2O$, from Schuchardt, soluble at least 24 parts at 25°, passed readily through the rubber.

Pyrogallol, $C_6H_3(OH)_3$, from Kahlbaum, freely soluble in acetone, passed readily through the septum. The last five substances named all contain a benzene ring in their structure, and it is but natural for them to be imbibed by an aromatic hydrocarbon septum such as vulcanized caoutchouc. Triphenylmethane, in particular,

dissolves in benzene and crystallizes from it with three molecules of benzene of crystallization.

Summary.

The results of the foregoing investigations may be summed up as follows.

1. The following substances in acetone solutions passed through vulcanized caoutchouc readily:- zinc chloride, cobaltous chloride, mercuric chloride, phosphorous trichloride, antimony trichloride, ferric chloride, potassium iodide, mercuric iodide, silver nitrate, cadmium bromide, lithium salicylate, camphoric acid, triphenylmathane, phthallic anhydride and pyrogallol.

2. The following substances in acetone solution passed through vulcanized caoutchouc sparingly:- malic, oxalic, citric, succinic, tartaric, and boric acids; lithium chloride, zinc acetate and mercuric cyanide.

The permeability of caoutchouc for any substance depends not upon the porosity of the rubber,nor upon the crystalline nature of the substance, but upon the affinity of rubber for that substance. If the caout-

chouc imbibes the substance, and there is on the other side of the septum a solvent, it passes through and osmosis occurs. If there is no solvent for it it passes into but not through the rubber, as would be the case of toluene separated by caoutchouc from water. And if the membrane has no affinity for the substance in contact with it then there is no chance at all for any osmosis to occur, and none does occur.

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